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Recent developments for biodiesel production by ultrasonic assist transesterification using different heterogeneous catalyst: A review

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ABSTRACT

Biodiesel is mainly produced by transesterification reaction between lipid feedstock such as vegetable oil or algal oil and alcohol. Considering the depletion of conventional fossil fuel, biodiesel is gaining more attention as a renewable, sustainable and environmental friendly fuel. Heterogeneous catalysts are mostly applied in transesterification reaction due to many advantages such as easy catalyst separation and reusability, improved selectivity, reducing process stages and cost effective. Biodiesel process faces various problems related to immiscible nature of oil and alcohol leads to poor mass transfer rate. This requires long reaction time, higher catalyst consumption, higher methanol-oil molar ratio, high temperature and high stirring rate. This review discusses that the latest advances in ultrasonic assist transesterification reaction with the use of heterogeneous catalysts to produce biodiesel with cost effective. Ultrasonic energy can emulsify the reactants to reduce the catalyst requirement, methanol-oil ratio, reaction time and reaction temperature.

Contents

1. Introduction

Due to the limited conventional fossil fuels, it has become necessary to find alternative clean and renewable energy resources. Biodiesel is a liquid fuel consisting of mono alkyl esters (methyl or ethyl) of long chain fatty acids derived from vegetable oils or animal fats or micro and macro algal oil. It is a kind of bio-energy as a substitute for conventional petro diesel fuel [1]. Biodiesel is known as an alternate to conventional petro diesel due to its renewability and better combustion performance properties [2]. It is an environmental friendly biodegradable fuel. Besides being a non toxic, it is free from sulfur and aromatics components and becoming a cleaner burning fuel than petroleum diesel. Biodiesel can be mixed with petroleum fossil fuel at any weight ratio or percentage, and it can be used without blending with fossil fuel (B100) as a successful fuel [3]. It has similar properties (physical and chemical) of petroleum diesel fuel. However, biodiesel properties have been found to be superior when compared to conventional fossil fuel. It has higher flash point, better cetane number and specific gravity, ultra-low sulphur concentration and better lubricating efficiency [4]. The standards (ASTM and EN) for biodiesel and petroleum based diesel are represented in Table 1 for the comparison.

Biodiesel is normally produced by the transesterification of the waste vegetable oil, algal oil or animal fat as a feedstock. The most commonly used alcohol is methanol or ethanol to produce methyl esters or ethyl esters. It is generally referred as fatty acid methyl esters (FAME) or fatty acid ethyl esters (FAEE) [5]. Nowadays, there are four different methods are available to reduce the viscosity of vegetable or algal oil such as Blending of oil with petroleum diesel, pyrolysis (Thermal Cracking), emulsification and transesterification [6]. The diesel combustion engines to be

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Table 1
Comparison of the standards for diesel and biodiesel based on American Society for Testing and Materials (ASTM) and European Standard (EN).

Properties	Units	Diesel		Biodiesel	
Specification		ASTM D975	EN590	ASTM D6751	EN14214
Applied to		Diesel	Diesel	FAAE	FAME
Density @ 15 °C	g/cm^3	0.85	0.82–0.845		0.86–0.9
Viscosity @ 40 °C	mm^2/s	2.6	2–4.5	1.9–6	3.5–5
Flash point	°C	59	55 min	93 min	120 min
Sulphur	mg/kg	50 max	350 max	15 max	10 max
Water	mg/kg	50 max	200 max	500 max	500 max
Cetane number		48 min	51 min	47 min	51 min
Sulphated ash	%mass	–	–	0.02	0.02
Cu corrosion	3 h/50 °C	1	1 max	3 max	1 max
Acid value	mgKOH/g	–	–	0.5 max	0.5 max
Methanol	%mass	–	–	0.2 max	0.2 max

modified to avoid carbon deposition, when the vegetable oil is used directly or mixed along with petroleum diesel [7,8]. The pyrolysis and emulsification methods are producing heavy carbon deposits, incomplete combustion, increase of lubricating oil viscosity and undesirable side products such as aliphatic and aromatic compounds and carboxylic acids [9,10].

Recently, transesterification has been reported as the most common way to produce biodiesel from vegetable or algal oil with alcohol usually methanol or ethanol, in presence of an acid or base catalyst [11]. The general scheme of the transesterification reaction for FAME and FAEE is presented in Eq. (1a), (1b), where R is a mixture of fatty acid chains [12].

$$\begin{array}{llcll} CH_2-O-CO-R_1 & & & CH_2-OH & R_1-COOCH_3 \\ | & & \text{Catalyst} & | & \\ CH-O-CO-R_2+3CH_3OH & & \leftrightarrow & CH-\ OH+R_2-COOCH_3 & \\ | & & & | & \\ CH_2-O-CO-R_3 & & & CH_2-OH & R_3-COOCH_3 \\ \text{Triglyceride} & \text{methanol} & & \text{Glycerol} & \text{methylester} \end{array} \tag{1a}$$

$$\begin{array}{llcll} CH_2-O-CO-R_1 & & CH_2-OH & R_1-COOC_2H_5 & \\ | & & \text{Catalyst} & | & \\ CH-O-CO-R_2+3C_2H_5OH & & \leftrightarrow & CH-OH+R_2-COOC_2H_5 & \\ | & & & | & \\ CH_2-O-CO-R_3 & & CH_2-OH & R_3-COOC_2H_5 & \\ \text{Triglyceride} & \text{ethanol} & & \text{Glycerol} & \text{ethylester} \end{array} \tag{1b}$$

Eqs. (1a) and (1b) show general stoichiometric equation for the transesterification of glyceride to biodiesel. (a) FAME (b) FAEE.

The catalyst presence is necessary to increase the reaction rate and the transesterification reaction conversion yield. The catalysts mainly used for the transesterification reaction are classified as homogeneous or heterogeneous catalyst. Homogeneous catalysts act in the same liquid phase as the reaction mixture. The homogeneous catalytic transesterification reaction is having more problems. It generates the soap formation and water formation. The soap and water formation consume more catalyst and reduce the biodiesel yield. In large scale biodiesel production using homogeneous catalyst, additional water for washing and separation process equipments required and consequent waste water treatment of the effluent adds to the overall process cost [13]. The heterogeneous catalysts act in a different phase from the reaction mixture (i.e., solid and gases). Heterogeneous catalyst transesterification reaction process requires less number of unit operations, with simple product separation and purification steps and without neutralization process [14]. The heterogeneous catalytic transesterification is included under Green Technology due to the following attributes: The catalyst can be reused, there is no water formation during the process and separation of biodiesel from glycerol is much easier than homogeneous catalyst process [15]. Dossin et al. [16] introduced the first heterogeneous catalytic transesterification pilot plant using MgO as catalyst with triolin and methanol as feedstock.

There are several techniques investigated for the transesterification reaction using heterogeneous catalysts for biodiesel production as followed: transesterification via radio frequency microwave, alcohol reflex temperature, alcohol supercritical temperature and ultrasonication. Recent developments of ultrasonic assisted technology have more benefits for transesterification reaction when compared with other technique. The present review discusses related to several heterogeneous catalysts used in the transesterification reaction for biodiesel production. This review aims to improving the understanding of ultrasonic assisted transesterification and their effects on biodiesel production process with heterogeneous catalysts to meet specific requirements in the process and also deals with the analysis of various heterogeneous catalyst used for biodiesel production.

2. Raw materials used for biodiesel production

Availability and types of the feedstock, production techniques, catalyst and operation cost are contributed to the overall cost of biodiesel production [17]. The selection of oil for biodiesel production is based on its availability, characteristics such as stability and cold flow property and cost [18]. Edible oils (rapeseed and soybean) are used for biodiesel production in Europe and united state of America. Philippines and Malaysia (leading Asian countries) also utilizing edible oil such as coconut oil and palm oil, respectively, for biodiesel production. The raw materials exploited commercially by some developed countries are edible oils such as soybean, rapeseed, palm, coconut, sunflower and linseed oils. The percentage of raw materials utilized for world commercial biodiesel production is rapeseed oil 84%, sunflower oil 13%, palm oil 1%, soybean oil and others 2%. The main raw material used in India is jatropha as non edible oils [19]. In an attempt to reduce the cost of biodiesel, micro and macro algae oils have also been tried by researchers as a source of feedstock for the production of biodiesel due to their higher biomass production, faster growth and photosynthetic efficiency as compared to other energy crops. Nowadays, each and every country is doing investigation to increase the growth rate of algal as a biomass and lipid content for biodiesel production. Balezentiene et al., studied that methodology for environmentally companionable bioenergy production as well as gives practical examples of environmentally valuable approaches based on practical experience or scientific knowledge. The main approaches to ahead maximum environmental and energetic assistance from bioenergy [20]. Table 2 shows the different raw materials commonly used for biodiesel production and their oil yield.

Leung and Guo [21] compared the transesterification reaction conditions for fresh canola oil and used frying oil. Higher molar ratio (7:1, methanol/used frying oil), higher temperature (60 °C) and higher amount of catalyst (1.1 wt% NaOH) was maintained in used frying oil when compared to fresh canola oil where optimal conditions maintained were 315–318 K, 1.0 wt% NaOH and 6:1

Table 2
Different feedstocks and their oil yield for biodiesel production.

Crops		Algae	
Name	Oil yield (%)	Species	Oil yield (%)
Babassu oil (*Attalea speciosa*)	60–70	*Botryococcus bruanii*	25–75
Borage oil (*Borago officinalis*)	20	*Chlorella* sp.	28–32
Camelina oil (*C. sativa*)	38–40	*Crypthecodinium cohni*	20
Castor oil (*Ricinus communis*)	45–50	*Cylindrotheca* sp.	16–37
Cuphea oil (*Cuphea viscosissima*)	25–43	*Nitzschia* sp.	45–47
Hemp oil (*Cannabis sativa*)	33	*Phaeodactylum tricornutu*	20–30
Jatropha oil (*J. curcas*)	45	*Schizochytrium* sp.	50–77
Jojoba oil (*Simmondsia chinensis*)	44	*Tetraselmis sueci*	15–23
Karanja oil (*P. pinnata*))	27–39	*Isochrysis galbana*	30–41
Linseed oil (*Linum usitatissimum*)	37–42	*Pavlova lutheri*	35.5
Neem oil (*Azadirachta indica*))	40–50	*Nannochloropsis* sp.	31–68

methanol/oil molar ratio. However, less reaction time (20 min) was observed for used frying oil when compared to fresh canola oil reaction time (60 min).

Non-edible oils with higher free fatty acids such as *Jatropha curcas* (Jatropha), *Ficus elastica* (rubber), *Camelina sativa* L. Crantz (*Camelina*), *Madhuca indica* (mahua), *Pongamia pinnata* (karanja), *Nicotina tabacum* (tobacco), *Calophyllum inophyllum* (polanga), etc., are used for transesterification. The fatty acid composition of Jatropha oil is similar to other edible oils. The presence of some toxic material in kernel (e.g., curcin) renders the oil to be not suitable for cooking purposes. The oil content in Jatropha seed is varying from 25% to 40% by weight and varying from 45% to 60% in kernel itself [22]. Miao and Wu [23] studied production of biodiesel from microalgae *C. protothecoides* using 100% catalyst (based on oil weight) and 56:1 M ratio of methanol to *C. protothecoides* oil at the temperature of 30 °C in 4 h of reaction time. The biodiesel specific gravity was reduced from an initial value of 0.912 to a final value of 0.8637 in 4 h of reaction time.

Algae have long been recognized as potentially good sources for biodiesel production because of their high lipid content and rapid biomass production [24]. Algae as a feedstock for biodiesel have been reviewed extensively in recent years [25]. Algae biomass can play an important role to solve the problem in producing biodiesel from vegetable sources in the near future. Algae appear to be the only source of renewable biodiesel that is capable of meeting the global demand for transport fuels. The cultivation of algae does not need much land as compared with terraneous plants [26]. Algae are photosynthetic microorganisms that convert sunlight, water and CO_2 to algal biomass [27]. Microalgae are classified as green algae (*chlorophyceae*), goldenbrown (*chrysophyceae*), diatoms (*bacillariophyceae*) and blue-green algae (*cyanophyceae*) [28].

Benemann [29] reported that total world commercial micro algal biomass production is about 10,000 t/year. Microalgae have much higher growth rates and productivity when compared to conventional agricultural crops, forestry and other aquatic plants. Algae requires much less land than other biodiesel feedstocks of land crops, up to 49 or 132 times less when compared to rapeseed or soybean crops [30]. Algae have the potential to dwarf all other biodiesel feedstocks due to their efficiency in photosynthesizing using solar energy [31]. Plants can collect a maximum of 5% of the solar energy over a 3 month period. The best algal biomass yields under tropical conditions are about 50 t/ha/year [32].

Currently, suspend-based open ponds and enclosed photobioreactors are generally used for algal biomass production to get biofuels [24]. At present, open ponds are used for the production of 98% of profitable algae biomass. After separating high value nutritional products present in the biomass are utilized for the production of biofuels [33]. Open ponds are having high efficiency and cost-effective for cultivating of algae biomass, but they are contaminated with surplus species very quickly [34]. Continuous open pond production has been successful for a limited number of algae such as *Chlorella, Spirulina* and *Dunaliella* (grown at high pH and NaCl concentration) [35]. In commercially operated open ponds, yield covers a range from 3.5 to 30 Mg dry weight per hectare per year with highest productivity under tropical or subtropical conditions. The extreme conditions in the raceway ponds are not favorable to increase yield [36].

Microalgae production in closed photobioreactors is highly expensive. Closed systems are much more expensive than open ponds. However, the closed system requires much less agricultural land and light energy to grow the microalgae. Photobioreactors offer a closed culture environment, which is protected from invading microorganisms, where temperatures are controlled along with an enhanced CO_2 fixation by bubbling through culture medium [37]. Maximum productivity can be achieved in a closed photobioreactor when compared to open pond due to higher surface-to-volume ratio. But in large scale of both open pond and closed photobioreactors, maximum of 100 g of biomass per square meter per day can be produced due to limited amount of incident sunlight on the Earth's surface [38].

Biodiesel production using algal farming offers many advantages such as the high growth rate of algae makes it possible to satisfy the huge demand on biodiesel using limited land resources, Cultivation of algae consumes less water than land crops, minimization of nitrous oxide release, mitigation of CO_2 and cost effective [39]. A major problem with the culture of algae in ponds or tanks is the harvesting of the algae. The drying operation for large water content of harvested algal biomass leads to energy-consuming process [40]. This problem was observed at the University of Florida when algae were being cultured in managed ponds for the production of nutrients for hogs. After 2 years with a lack of success, the algal-nutrient culture was abandoned [41].

Various researchers reported that algae might be better for higher biodiesel production [42]. Conversely, algal biodiesel technology has not yet been developed to the point of full commercial scale production, but working feasibility studies have been conducted to arrive the full scale commercial production. Specially bred mustard varieties can produce high oil yields. The left over meal after the oil has been pressed out can act as an effective and biodegradable pesticide [43]. Algae contain lipids and fatty acids as sources of energy. Algae present an exciting possibility as a feedstock for biodiesel. Algae contain anywhere between 2 and 40 weight percentage of oils [44]. The oil contents of some microalgae are given in Table 2.

The lipid and fatty acid contents of algae vary in accordance with culture conditions. Algal oil contains saturated and monounsaturated fatty acids. The algal oil fatty acids were determined in the following proportions: oleic acid (36%), palmitic acid (15%), stearic acid (11%), iso—17:0 (8.4%) and linoleic acid (7.4%). The high proportion of saturated and monounsaturated fatty acids in this algal is considered to be optimal from a fuel quality perspective [45].

The major crisis associated with the use of algal oils as fuels for diesel engines is caused by high fuel viscosity in compression ignition. Due to their low volatility and high viscosity about 10–20 times higher than diesel fuel, they do not burn completely and form deposits in the fuel injector of diesel engines [46]. The

transesterification of algal oils will significantly reduce the original viscosity and increase the fluidity [26]. The physical and fuel properties of biodiesel from algal oil (e.g., density, viscosity, flash point, heating value, etc.) are comparable with petro diesel fuel [47]. Xu et al. [48] discussed the fuel characteristics of biodiesel obtained from the acidic transesterification of heterotrophic microalgae oil with methanol. The biodiesel was characterized by a density of 0.864 kg/L, a high heating value of 41 MJ/kg and a viscosity of 5.2 mm^3/s at 40 °C. Vijayaraghavan and Hemanathan [49] investigated the fuel characteristics of biodiesel derived from freshwater algae as density of 0.801 kg/L, flash point of 371 K, pour point of 259 K, cetane number of 52, minimum gross calorific value of 40 MJ/kg, ash content of 0.21% and water content of 0.02 vol%.

3. Transesterification reaction for biodiesel production

The viscosity of the vegetable and algal oil is not suitable for the combustion engines. Direct usage of vegetable oils causes poor atomization of the fuel in the engine's combustion chamber. High viscosity of oils should be reduced before used in universal diesel engine. The least four possible methods investigated for biodiesel production from vegetable and algal oil are blending with petro diesel, micro-emulsification, pyrolysis and transesterification [50]. Transesterification reactions are developed to produce cleaner and environmental friendly safe fuel oil. Pyrolysis and micro-emulsion are costly process which yield low quality biodiesel when compared to transesterification process [51].

The transesterification reactions were analyzed with several feedstocks to ensure the quality of biodiesel by enhancing the physicochemical properties [52]. The mechanism of transesterification reaction is presented in Eq. (2a), (2b), (2c). Transesterification consists of a number of consecutive and reversible reactions. In presence of methanol and catalyst, Triglycerides are converted in stepwise to diglycerides (DG), monoglycerides (MG) and finally glycerol [53]. In each step, a mole of fatty acid methyl ester is liberated.

$$\begin{array}{llll} CH_2-O-CO-R_1 & & & CH_2-OH \\ | & \text{Catalyst} & & | \\ CH-O-CO-R_2+CH_3OH & \leftrightarrow & CH_3-O-CO-R_1+ & CH-O-CO-R_2 \\ | & & & | \\ CH_2-O-CO-R_3 & & & CH_2-O-CO-R_3 \\ \text{Triglyceride} \quad \text{methanol} & & \text{Methylester} & \text{diglyceride} \end{array} \tag{2a}$$

$$\begin{array}{llll} CH_2-OH & & & CH_2-OH \\ | & \text{Catalyst} & & | \\ CH-O-CO\text{-}R_2+CH_3OH & \leftrightarrow & CH_3-O-CO-R_2 & +CH-OH \\ | & & & | \\ CH_2-O-CO-R_3 & & & CH_2-O-CO-R_3 \\ \text{Diglyceride} \quad \text{methanol} & & \text{Methylester} & \text{monoglyceride} \end{array} \tag{2b}$$

$$\begin{array}{llll} CH_2-OH & & & CH_2-OH \\ | & \text{Catalyst} & & | \\ CH-OH+CH_3OH & \leftrightarrow & CH_3-O-CO-R_3+ & CH-OH \\ | & & & | \\ CH_2-O-CO-R_3 & & & CH_2-OH \\ \text{Monoglyceride} \quad \text{methanol} & & \text{Methylester} & \text{glycerol} \end{array} \tag{2c}$$

Eq. (2) shows mechanism of transesterification. [53].

4. Heterogeneous catalytic transesterification

During homogeneous catalytic transesterification reaction, oil (vegetable or algal oil) with higher fatty acid leads to the soap and water formation, oil losses, separation problem and increase in biodiesel production cost. The major drawback of homogeneous catalyst such as KOH and NaOH is hygroscopic nature and hazardous for the environment as compared to the heterogeneous catalyst [54]. Heterogeneous catalytic reaction converts triglycerides into methyl ester and glycerol as a byproduct slowly but produced biodiesel in a very feasible economic way due to the reusability of catalyst for both batch and continuous process and cost effective due to easy separation [55]. Catalysts are generally classified in to homogeneous, biocatalyst and heterogeneous catalyst [56–58] and their sub classification also listed in the flow chart (Fig. 1).

Different heterogeneous catalytic transesterification for various feedstocks are summarized (Table 3) along with process conditions. The effectiveness of the heterogeneous catalytic reaction is based on the activity of the solid catalyst used. There are two types of heterogeneous catalyst used for biodiesel production such as base and acid catalyst. The reaction time and temperature is maintained in lower range for solid base catalytic transesterification reaction [59]. The solid base catalyst is found to be more active when compared to acid catalyst.

Generally, metal oxides group are studied for transesterification reaction. There are several metal oxides studied: magnesium oxide (MgO), calcium oxide (CaO), barium oxide (BaO), strontium oxide, titanium oxide, zinc oxide, mixed oxides catalysts and hydrotalcites [60]. MgO, CaO, SrO and BaO are widely used as a alkaline earth metal. These are having well heterogeneous in nature. Calcium oxide is much attracted due to its availability and cost effective. CaO (from waste eggshell) prepared by calcinations is used as a base catalyst for biodiesel production. Cho YB et al. [65] reported that palm oil was converted to biodiesel and achieved 98 wt% at the temperature of 65 °C in 2 h using 10 wt% of CaO and Methanol to oil molar ratio of 18:1.

Magnesium oxide prepared by direct heating of magnesium carbonate or magnesium hydroxide, has the weakest basic strength and solubility in methanol among group II oxides. Di Serio et al. [66] reported 92% biodiesel yield with MgO catalyst, using 12:1 methanol (MeOH) to oil molar ratio with 5.0 wt% of the catalyst at methanol supercritical condition in 1 h. Wen et al. [70] carried out transesterification from waste cooking oil with methanol at 170 °C in 6 h with 10 wt% of MgO/TiO_2 and 50:1 M ratio of MeOH and oil. Xu et al. [71] synthesized KF/Zn(Al)O catalyst. The catalytic activity of KF/Zn(Al)O was analyzed and

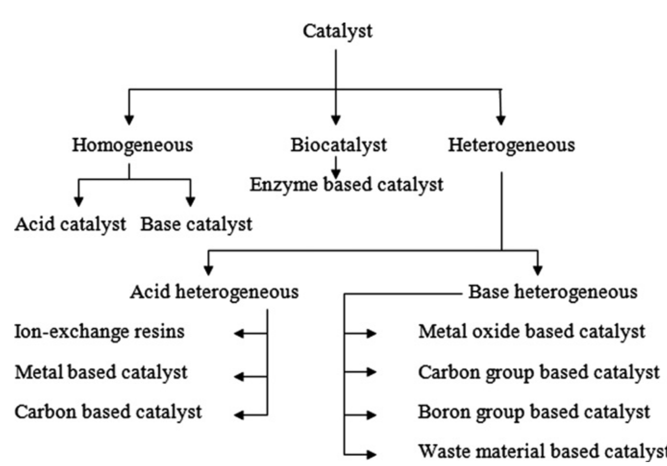


Fig. 1. Classification of catalyst.

Table 3
Different heterogeneous catalyst for transesterification reaction: feedstock, optimum parameter condition and biodiesel yield.

Feedstock	Catalyst	Optimum reaction condition	Yield (wt%)	Reference
Sunflower oil	Fe–Zn double metal cyanide (DMC)	Cat. = 3 wt%, MeOH/Oil = 15:1, T = 170 °C, t = 8 h	92	[61]
Sunflower oil	ZrO_2 supported La_2O_3 catalyst	Cat. = 2 wt%, MeOH/Oil = 3:1, T = 60 °C, t = 5 h	84.9	[62]
Soybean oil	ZnO loaded with $Sr(NO_3)_2$	Cat. = 5 wt%, MeOH/Oil = 12:1, T = 65 °C, t = 4 h	94.7	[63]
Soybean oil	S–ZrO_2	Cat. = 5 wt%, MeOH/Oil = 20:1, T = 120 °C, t = 1 h	98.6	[64]
Palm oil	CaO from eggshells	Cat. = 10 wt%, MeOH/Oil = 18:1, T = 65 °C, t = 2 h	98	[65]
Palm oil	CaO/Al_2O_3	Cat. = 1.3 wt%, MeOH/Oil = 12:1, T = 64.29 °C, t = 5 h	98.64	[67]
Palm oil	KF/Ca–Al hydrotalcite	Cat. = 4 wt%, MeOH/Oil = 12:1, T = 65 °C, t = 5 h	97.98	[68]
Rape seed oil	KNO_3/CaO	Cat. = 1 wt%, MeOH/Oil = 6:1, T = 65 °C, t = 3 h	98	[69]
Waste cooking oil	MgO/TiO_2	Cat. = 10 wt%, MeOH/Oil = 50:1, T = 170 °C, t = 6 h	91.6	[70]
Jatropha oil	Mg–Al hydrotalcite	Cat. = 1 wt%, MeOH/Oil = 4:1, T = 45 °C, t = 1.5 h	95.2	[71]
Soybean oil	Sodium silicate	Cat. = 3 wt%, MeOH/Oil = 7.5:1, T = 60 °C, t = 1 h	≈ 100	[74]
Moringa oleifera oil	SO_4^{2-}/SnO_2-SiO_2	Cat. = 3 wt%, MeOH/Oil = 19.5:1, T = 150 °C, t = 2.5 h	84	[75]
Mixed waste vegetable oil	$Al(HSO_4)_3$	Cat. = 0.5 wt%, MeOH/Oil = 16:1, T = 220 °C, t = 50 min	81	[82]
Purified palm oil	SO_4–ZrO_2	Cat. = 0.5 wt%, MeOH/Oil = 25:1, T = 250 °C, t = 10 min	90	[83]
Sunflower oil	$SO_4^{2-}/ZrO_2/SiO_2$	Cat. = 14.6 wt%, Ethanol/Oil = 12:1, T = 200 °C, t = 6 h	91.5	[84]
Cottonseed oil	Carbon based solid acid	Cat. = 0.2 wt%, MeOH/Oil = 16.8:1, T = 220 °C, t = 4.5 h	94.8	[85]
Croton megalocorpus oil	SO_4^{2-}/SnO_2-SiO_2	Cat. = 3 wt%, MeOH/Oil = 15:1, T = 180 °C, t = 2 h	95	[86]
Yellow horn (Xanthoceras sorbifolia Bunge.)	Heteropolyacid (HPA)- $Cs_{2.5}H_{0.5}PW_{12}O_{40}$	Cat. = 1 wt%, MeOH/Oil = 12:1, T = 00 °C, t = 10 min	96.22	[87]

compared with Zn(Al)O and KF/ZnO. It was found that the prepared KF/Zn(Al)O catalyst had the highest activity than that of Zn–Al hydrotalcite compounds. This catalyst was particularly effective in transesterification for a methanol to oil molar ratio of 6:1, 3 wt% of KF/Zn(Al)O catalysts at 65 °C reaction temperature with the biodiesel yield obtained as 95 wt% at a reaction time of 3 h.

Deng et al. [72,73] discussed that solid base nanocatalyst derived from hydrotalcites with 3:1 M ratio of Mg/Al was synthesized by co-precipitation method using urea as precipitator with microwave hydrothermal treatment followed by calcination. The catalyst size was calculated as 7.3 nm, but according to atomic force microscope (AFM) analysis, they congregated to form a layered structure with size as large as 0.941 µm width and 381 nm thickness. This catalyst was used for the transesterification of Jatropha oil containing 5–12 acid values for biodiesel production after pretreatment. Guo et al. [74] studied the optimization of the methyl ester yield produced via transesterification of soybean oil using sodium silicate as a catalyst. The optimum reaction conditions obtained were approximately as 7.5:1 M ratio of alcohol/oil, 3 wt% catalyst amount, 1 h reaction time and 60 °C reaction temperature under the FAME approximate yield of 100%.

Solid acid heterogeneous catalysts have several advantages over solid base catalyst. The reaction is less affected by the presence of free fatty acid and water. It has good ability to carry out the esterification of free fatty acid [76]. The major drawback of the base catalyst discussed is its unsuitability towards high FFA content feedstock. Soaps and water can be produced using base as a catalyst. In this regard, the feedstock would need to be pretreated in order to reduce its high FFA content. The acid solid catalyst introduced as heterogeneous catalyst such as Ion-exchange resins, carbon based acid catalyst and aluminum based acid catalyst. Currently, all researchers focused on exploring new and sustainable solid acid catalysts for biodiesel production. In addition, it is understood that solid acid catalysts have the strong potential to replace liquid acid catalyst [77]. The main advantages of using solid acid catalyst are (1) esterification and transesterification occurs simultaneously, (2) they are insensitive to free fatty acids content [78], (3) eliminate the washing step in biodiesel process [79], (4) easy separation of the catalyst from the reaction mixtures resulting in lower product contamination level, (5) easy regeneration and recycling of catalyst and (6) reduction in corrosion problem, even with the presence of acid species [80]. The ideal solid acid catalyst for transesterification reaction should have characteristics such as an interconnected system of large pores, a hydrophobic surface and high concentration of strong acid sites [81].

Conversely, research on direct use of solid acid catalyst for transesterification reaction has not been widely explored because of its limitation with slow reaction rate and possible undesirable side reactions. Moreover, there is a knowledge gap on the fundamental studies dealing with reaction pathway of triglycerides on solid acids. The following section will give an overview of various solid acid catalysts reported for biodiesel production. Ramachandran et al. [82] prepared the heterogeneous acid catalyst $Al(HSO_4)_3$ through the sulfonation of anhydrous $AlCl_3$. This catalyst was employed to synthesis methyl ester from mixed waste vegetable oil with methanol. The maximum conversion of triglyceride was achieved as 81 wt% with 50 min reaction time at 220 °C, 16:1 M ratio of MeOH to oil and 0.5 wt% of catalyst. The high catalytic activity and stability of this catalyst was related to its high acid site density, hydrophobicity that prevented the hydration of –OH group and hydrophilic functional groups (–SO_3H) that gave improved accessibility of MeOH to the triglyceride.

Shu et al. [85] prepared carbon based acid catalyst and used for transesterification of cotton seed oil to obtain 94.8 wt% of methyl ester at 220 °C in 4 h reaction time and methanol to cotton seed oil molar ratio of 16.8:1 and 0.2 wt% of catalyst. Dehkhoda et al. [88] achieved 92% biodiesel yield from canola oil with biochar based solid acid catalyst at operating conditions of 60°C reaction temperature, molar ratio of MeOH to oil as 15:1, 5 wt% of catalyst and reaction time as 15 h. Shu et al. [89] prepared a carbon-based solid acid catalyst through the sulfonation of carbonized vegetable oil asphalt. This catalyst was used to produce biodiesel (by simultaneous esterification and transesterification reaction) from waste vegetable oil with high free tatty acid content. The maximum conversion of triglyceride and FFA was reached as 80.5 wt% and 94.8 wt% with 4.5 h of reaction time at 220 °C, 16.8:1 M ratio of methanol to oil and 0.2 wt% of catalyst.

5. Ultrasonic assisted transesterification using heterogeneous catalyst

Triglycerides and alcohols are immiscible with each other. The transesterification reaction takes place at the interface of the two phases such as liquid-liquid heterogeneous and it causes very slow reaction. This reaction can be catalyzed by alkali, acid or enzyme, each catalyst has its own advantages and disadvantages.

In the case of enzyme catalyzed reaction using lipase as a catalyst, side reactions do not proceed [90]. But the lipase is very expensive for industrial scale production. Acid catalyzed processes are useful when a large amount of free fatty acids is present in the vegetable and algal oil. But the reaction time is very long (48–96 h), even the boiling point of the alcohol and required molar ratio of alcohol to oil is very high (20:1 of alcohol/oil) [91].

At present, the transesterification reaction with supercritical methanol was carried out without any catalyst. Saka and Kusdiana [92] reported that the supercritical methanol process has several advantages such as short reaction time and a simple purification procedure without any catalyst. In addition, Barbosa et al. [93] studied the use of microwave irradiation for solid catalyzed transesterification, where the reaction was completed in 1–2 min. But the limitation of these techniques leads to high energy consumption for maintaining higher temperature condition. On the other hand, it is also very important to find a more effective catalyst for the transesterification.

Toda et al. [94] found a new solid catalyst consisting of stable sulphonated amorphous carbons, which have much higher activity than conventional solid acid catalysts. The reaction of triglyceride with alcohol can only occur in the interfacial region between the two immiscible liquids so that a vigorous mixing is required to increase the area of contact between the reaction mixtures. It has been known that ultrasonic irradiation of a liquid produces acoustic cavitations resulting in fast mixing in the liquid. Davidson et al. reported that hydrolysis of oils, fats and waxes in aqueous NaOH was improved by using acoustic cavitations [95]. This would be due to the collapse of cavitation bubbles and the formation of emulsification through the ultrasonication [96]. The ultrasonic irradiation in the chemical processing enhances both the mass transfer and chemical reactions. It offers the potential for shorter reaction times, cheaper reagents and less insignificant physical conditions, leading to less expensive and smaller chemical plants.

Newly, the use of ultrasound has gained interest in biodiesel production. Ultrasonication (ultrasound) is producing a sound wave with a frequency higher than human audibility limits [97]. Ultrasound provides the mechanical energy for mixing and the required activation energy for initiating the transesterification reaction [98]. Thence, the reaction time is shortened and the biodiesel yield is increased [99–102]. The ultrasound phenomenon has its own physical and chemical effects on the liquid-liquid heterogeneous reaction system through cavitation bubbles following the principles as follows [103]: (1) the chemical effect, in which radicals such as H^+ and OH^- are produced during a transient implosive collapse of bubbles (in a liquid irradiated with ultrasound) that accelerate chemical reaction in the bulk medium; (2) the physical effect of emulsification, in which the micro-turbulence generated due to radial motion of bubbles leads to intimate mixing (homogenize the mixture) of the immiscible reactants. Considering all these principles, the interfacial region between the oil and alcohol intensively increases, resulting in faster reaction kinetics and higher conversion of oil and product yield.

The ultrasonication reactor was first introduced by Hielscher Ultrasonic GmbH for biodiesel production in the year 2000 onwards. The Hielscher ultrasonic reactor adopts an ultrasonic processor, which operates at an ultrasonic frequency ranged from 18 to 20 kHz. Ultrasonic waves at this frequency create an intense cavitation in liquids. The collapse of the cavitation bubbles creates emulsification of immiscible liquids. Nishimura et al. [104] have investigated the transesterification of vegetable oil using low frequency ultrasound (28–40 kHz). An excellent yield ($\approx$98%) was obtained at a 28 kHz ultrasound while a significant reduction of reaction time was obtained by using a 40 kHz ultrasound. Colucciet.al. [105] hypothesized that the observed mass transfer and kinetic rate enhancements were mainly caused by the increase in interfacial area and activity of the microscopic and macroscopic bubbles formed when ultrasonic waves of 20 kHz were applied to the two-phase reaction system. It is important to note that the processing time is reduced to less than 30 s, and the separation time is reduced to less than 60 min by using the ultrasonic reactor.

The ultrasonic reactor is also capable of delivering a biodiesel yield of 99% [106] at a reduced amount of catalyst and methanol required in the reaction. Furthermore, Hielscher ultrasonic reactor shows outstanding energy efficiency, when compared to high-shear mixing and hydrodynamic cavitation. The Hielscher ultrasonic reactor requires 1.4 kW h/m^3 (approximately) for biodiesel production. However, the hydrodynamic magnetic impulse cavitation requires 32.0 kW h/m^3 (approximately) and the high-shear mixing requires 4.4 kW h/m^3 (approximately) [107] to achieve the related result.

Reaction parameters and results of some studies that are focused on the use of heterogeneous catalysts in combination with ultrasonic irradiation are summarized in Table 4. As concluded from this table, the biodiesel yields achieved were generally high and comparable with those of homogenous catalysts. Conversely, the reaction temperatures were slightly higher while the reaction times were longer. Catalyst loading under ultrasonic field is usually higher than that for homogenous catalysts but this does not significantly affect the economics of the process because of simple separation and reusability of catalyst. Production of biodiesel from palm oil using SrO and BaO as heterogeneous catalysts has been performed by Salamatinia et al. [108]. They used ultrasonic assisted transesterification process to improve reaction rate and to study the effects of ultrasonic waves on the reaction parameters. They reported that the basic properties of the catalyst were the main cause for their high activity. The results showed that the low frequency ultrasonic assisted transesterification process had no significant mechanical effects on

Table 4
Performance of ultrasonic assisted transesterification reaction for biodiesel production using various heterogeneous catalysts.

Feedstock	Catalyst	Optimum reaction condition	Yield (wt%)	Reference
Palm oil	BrO and SrO	Cat.=2.8 wt%, Alcohol/Oil=9:1, T=65 °C, t=50 min, Frequency 20 kHz	$\approx$95	[108]
Palm oil	CaO	Cat.=3 wt%, MeOH/Oil=15:1, T=65 °C, t=60 min, Frequency 20 kHz	77.3	[109]
Palm oil	BaO	Cat.=3 wt%, MeOH/Oil=15:1, T=65 °C, t=60 min, Frequency 20 kHz	95.2	[109]
Palm oil	SrO	Cat.=3 wt%, MeOH/Oil=15:1, T=65 °C, t=60 min, Frequency 20 kHz	95.2	[109]
Frying oil	Mg-MCM-41,Mg-Alhydrotalcite,K/ZrO_2	MeOH/Oil=15:1, T=60 °C, t=6 h,	87	[110]
Jatropha curcus oil	Na/SiO_2	Cat.=3 wt%, MeOH/Oil=9:1, Low temperature, t=15 min, Frequency 24 kHz	98.53	[111]
Soybean oil	Immobilized novozym 435	Cat.=6 wt%, MeOH/Oil=6:1, T=40 °C, t=240 min, Frequency 40 kHz	96	[112]
Jatropha oil	Nano-sized Mg/Al oxide	Cat.=1 wt%, MeOH/Oil=4:1, T= 318 K, t=1.5 h, Ultrasonic power 210 W	95.2	[73]
Jatropha oil	Ca–Mg–Al	Cat.=1.5 wt%, MeOH/Oil=4:1, T=60 °C, t=30 min, Frequency 20 kHz	94.3	[113]
Jatropha oil	KF/CaO	Cat.=3 wt%, MeOH/Oil=12:1, T=65 °C, t=60 min, Frequency 40 kHz	99.6	[115]
Soybean oil	KF/γAl_2O_3	Cat.=3.5 wt%, MeOH/Oil=12:1, T=65°C, t=60 min, Frequency 53.3 W/dm^3	98.7	[115]

SrO. But BaO catalyst study confirmed that the ultrasonic significantly improved the process by reducing the reaction time to less than 50 min at a catalyst loading of 2.8 wt% to achieve biodiesel yield of higher than 95%. The optimum alcohol to oil ratio was observed as 9:1.

A new study on alkali earth metals was established by Mootabadi et al. [109]. The researchers investigated the effect of ultrasonic waves at 20 kHz and 200 W on the regenerated catalyst and made comparison between mechanical stirring and ultrasonic irradiation. They used palm oil in the production process and investigated the optimum conditions for the catalysts such as CaO, SrO and BaO. Ultrasonic irradiation showed great enhancements on the reaction parameters for the ultrasonic-assisted process, particularly for the obtained yield and reaction time. It was concluded that catalyst leaching was the main cause for the drop in activity in the case of regenerated catalyst. BaO catalyst was found to be stable during the leaching. Under the optimum conditions, 95.2% yield was achieved with 60 min of reaction time and 15:1 M ratio of methanol to oil for both BaO and SrO catalysts. For CaO catalyst, 77.3% yield was achieved with same condition as mentioned in the previous sentence. These results were found to be 30–40% more when compared to the corresponding results obtained using conventional stirring reactor system without ultrasonication.

Other types of heterogeneous catalysts were used for transesterification by Georgogianni et al. [110]. They investigated a wide range of catalysts including Mg-MCM-41, Mg–Al hydrotalcite and K^+-impregnated zirconium. The bases for the selection of these catalysts were found to be mesoporosity and surface basicity. The reaction mixture consisting of frying oils, methanol and the desired catalyst was mixed in a batch reactor through mechanical stirrer for 24 h and through ultrasonication for 5 h. The results suggested that the basic strength was the cause of the good activity of the catalysts. Mg–Al hydrotalcite achieved the highest reaction conversion of 87% at a reaction temperature of 60 °C. Thus, ultrasonic irradiation significantly enhanced the reaction rate causing a reduction in reaction time.

Kumar et al. [111] studied the performance of an immobilized catalyst and prepared a supported Na/SiO_2 catalyst to investigate the effects of ultrasonication on the transesterification process. Under the optimum conditions and with the use of Jatropha curcus oil as feed stock, the biodiesel yield was achieved as 98.53% with 15 min of reaction time. They found that the use of ultrasonic assisted transesterification process reduced the amount of catalyst that must be used in the process. They attributed that the effects of ultra sonic cavitation increases the surface area available for the reactants. That, in turn, increased the activity of the catalyst even at minimum catalyst dosage. As a result, the purity of glycerol which is the main byproduct of biodiesel production was increased. The researchers also investigated the reusability of the catalyst with the minimum five cycles, the reaction conversion showed minimal reduction.

Yu et al. [112] reported that biodiesel production from soybean oil was made by combining the different types of catalyst called as Novozym435 (Candida Antarctica lipase B immobilized on polyacrylic resin). The procedure was involved with the combination of the effects of both ultrasonic waves and mechanical vibration instead of mechanical stirring due to its detrimental effects on the catalyst. The researcher studied the effects of reaction parameters on the activity of the catalyst. The catalyst showed good stability with no loss of enzymatic activity after five successive cycles under ultrasonic irradiation. In spite of slightly longer reaction time, high production yield was obtained at low reaction temperature.

Deng et al. [72,73] prepared nano-sized mixed Mg/Al Oxides. Due to of their strong basicity, the nano particles were further used as catalyst for biodiesel production from Jatropha oil after pretreatment. Experiments were conducted with the solid basic catalyst in an ultrasonic transesterification reaction under different conditions. At the optimized condition, biodiesel yield of 95.2% was achieved. After removing the glycerol on the catalyst surface, the nano-sized mixed Mg/Al Oxides was reused for 8 times. It could be concluded that the calcinated hydrotalcite nanocatalyst combined with ultrasonic radiation is an effective method for the production of biodiesel from Jatropha oil.

Base solid catalysts have been used in several studies on low frequency ultrasonic assisted methanolysis of various oils such as Jatropha oil and waste soybean oil in batch reactors with the catalyst include Ca–Mg–Al [113], KF/CaO [114] and KF/γAl_2O_3 [115]. The activity of base solid catalysts is associated to their basic strength, so that the most basic catalyst showed the highest conversion. Deng et al. [113] reported optimum conditions for biodiesel production. The most effective base solid catalysts studied are BaO and Ca–Mg–Al hydrotalcite. The yield of 95% biodiesel from Jatropha oils was established with 30 min of reaction time. Ca–Mg–Al hydrotalcite could be reused twelve times after washing of the adsorbed glycerol from the surface of catalyst with ethanol. Qian et al. [114] have recently exposed the reaction mixture in the frequency range between 20 and 48 kHz. The biodiesel yield was found to be increased with increase in the ultrasonic intensity up to 1.01 W/cm^2. Ren et al. [115] newly discussed that the highest biodiesel yield of 98.7% was obtained at 53.3 W/dm^3 in the range of ultrasonic sound energy varied from 26.7 to 66.7 W/dm^3. Two possible sources cause the loss of efficiency in the ultrasonic waves transfer through the liquids: the coalescence of small cavitation bubbles into larger ones which act as a barrier to that wave's transfer and the decoupling effect. The wave frequency and specific ultrasonic energy influence the biodiesel yield in the continuous sonication method.

Comparison between the parameters of reactions listed in Table 4 under ultrasonic field with those in Table 3 for conventional processes for heterogeneous catalysts clearly shows the enhancements caused by ultrasonic irradiation. Reaction times and catalyst loadings of the ultrasonic assisted transesterification processes were shorter than those for the conventional transesterification processes. The molar ratio of methanol-oil was less than that of conventional processes and the production yields were higher. As a conclusion, with the use of ultrasonic, high activity of homogenous catalysts can be achieved using the more environmental friendly heterogeneous catalysts.

6. Conclusion

The biodiesel is a renewable, sustainable and clean alternative fuel for diesel engines. Biodiesel production by catalytic transesterification of vegetable and algal or animal fats with methanol is the excellent techniques. Transesterification reaction faces several problems related to the presence of FFA in the feedstock and the biphasic (immiscible) nature of the reactants such as methanol and oil. The presence of basic and acid sites on the surface of heterogeneous catalyst shows the best future development to produce biodiesel. Additionally, it allows for carrying out the biodiesel production process in a single step. The bifunctional solids and the strong acid heterogeneous catalysts are presented as the new way to develop the biodiesel production by transesterification reaction, for the reason that they can be catalyzed for both free fatty acids esterification reaction and triglycerides transesterification at the same time. Ultrasonic irradiation has been confirmed to be successfully used in a significant way to improve the emulsification of the reactants to increase the mass transfer rate during the transesterification reaction.

This improvement leads to reductions in reaction temperature, reaction time, alcohol to oil ratio and catalyst amount causing a significant decrease in the biodiesel production cost. Ultrasonic irradiation was tested for wide range of different heterogeneous catalysts with several feedstocks. That shows a potential result on the transesterification reaction variables when compared with the result of conventional homogeneous and heterogeneous catalytic process. Consequently, understanding of ultrasonic sound waves to accelerate the transesterification process could be of great future improvement for both batch and continuous production systems towards a more sustainable biodiesel production process.

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